

D E C L A R A T I O N



In the matter of U.S. Patent  
Application Ser. No. 10/009,488  
in the name of Rikiya YAMASHITA,  
et al.


I, Mariko ENDO, of Kyowa Patent and Law Office, 2-3,  
Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare  
and say:

that I am thoroughly conversant with both the Japanese  
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that the attached document represents a true English  
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filed on January 18, 2001.

I further declare that all statements made herein of  
my own knowledge are true and that all statements made on  
information and belief are believed to be true; and further  
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Inventor:

Address: c/o DAI NIPPON PRINTING CO., LTD.  
1-1, Ichigaya-Kaga-Cho 1-Chome, Shinjuku-Ku, Tokyo-To  
Name: Rikiya YAMASHITA

Inventor:

Address: c/o DAI NIPPON PRINTING CO., LTD.  
1-1, Ichigaya-Kaga-Cho 1-Chome, Shinjuku-Ku, Tokyo-To  
Name: Masataka OKUSHITA

Inventor:

Address: c/o DAI NIPPON PRINTING CO., LTD.  
1-1, Ichigaya-Kaga-Cho 1-Chome, Shinjuku-Ku, Tokyo-To  
Name: Kazuki YAMADA

Applicant:

Identification Number: 000002897  
Name: DAI NIPPON PRINTING CO., LTD.  
President: Yoshitoshi KITAJIMA

Agent:

Identification Number: 100111659  
Patent Attorney  
Name: Satoshi KANAYAMA

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[Title of Invention] LITHIUM ION BATTERY TAB

[Claims]

[Claim 1]

A lithium ion battery tab including a sealed package of a lithium ion battery having a peripheral part including the part holding the tab sealed by heat-sealing and a lithium ion battery module held in the package comprising at least a base layer, an adhesive layer, a layer treated by a chemical conversion treatment 1, aluminum, a layer treated by a chemical conversion treatment 2 and a heat-sealable layer, wherein

when heat-sealing the peripheral part of said lithium ion battery, at least the front, the rear and the side surfaces of the part to be heat-sealed are subjected to a chemical conversion treatment.

[Claim 2]

The lithium ion battery tab according to claim 1, wherein said chemical conversion treatment is a phosphate chromate treatment.

[Claim 3]

The lithium ion battery tab according to claim 1, wherein said chemical conversion treatment uses a resin containing a phenolic resin, and a metal of molybdenum, titanium or zirconium, or a metallic salt.

[Claim 4]

The lithium ion battery tab according to claim 1, wherein said chemical conversion treatment is a triazine thiol treatment.

[Claim 5]

A lithium ion battery tab including a sealed package of a lithium ion battery having a peripheral part including the part holding the tab sealed by heat-sealing and a lithium ion battery module held in the package comprising at least a base layer, an adhesive layer, aluminum, a layer treated by a chemical conversion treatment and a heat-sealable layer of an olefin resin, wherein when heat-sealing the peripheral part of

said lithium ion battery, at least the front, the rear and the side surfaces of the part to be heat-sealed are subjected to a chemical conversion treatment.

[Claim 6]

The lithium ion battery tab according to claim 5, wherein said chemical conversion treatment is a phosphor chromate treatment.

[Claim 7]

The lithium ion battery tab according to claim 5, wherein said chemical conversion treatment uses a resin containing a phenolic resin, and a metal of molybdenum, titanium or zirconium, or a metallic salt.

[Claim 8]

The lithium ion battery tab according to claim 5, wherein said chemical conversion treatment is a triazine thiol treatment.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a tab body of a lithium ion battery exhibiting stable sealability to a package.

[0002]

[Background Art]

Lithium ion batteries, which are also known as lithium secondary batteries, have a liquid or gelatinous polyelectrolyte, and generate a current by the migration of lithium ions. Lithium batteries include those provided with positive and negative electrode active substances formed of polymers.

The lithium secondary battery comprises a positive electrode collector (aluminum or nickel), a positive electrode active substance layer (metal oxide, carbon black, a metal sulfide, an electrolytic solution or a polymeric positive electrode material, such as polyacrylonitrile), an electrolytic layer (an electrolytic solution of propylene carbonate, ethylene carbonate, dimethyl carbonate or ethylene methyl carbonate, an inorganic solid electrolyte of a lithium salt or a gelled electrolyte), a negative electrode

active layer (lithium metal, an alloy, carbon, a liquid electrolyte or a polymer, such as polyacrylonitrile) and a negative collector (copper, nickel or a stainless steel), and the package containing these components.

Lithium batteries are used as power supplies for personal computers, portable remote terminals, such as pocket telephones and PDAs, video cameras, electric vehicles, industrial robots, artificial satellites and the like, and as energy storage batteries.

The package of the lithium ion battery is a cylindrical or parallelepipedic metal can formed by pressing a metal sheet or a pouch formed by working a packaging laminated structure consisting of an outermost layer, an aluminum layer and a sealant layer.

[0003]

[Problems to be Solved by the Invention]

However, packages for lithium batteries have the following problems. The metal can has rigid walls and hence the shape of the battery is dependent on that of the metal can. Since the hardware is designed so as to conform to the shape of the battery, the dimensions of the hardware are dependent on the shape of the battery, which reduces the degree of freedom of designing the shape of the hardware.

A package, such as a pouch made from a packaging laminated structure for holding a lithium ion battery module therein or an embossed package formed by pressing a packaging laminated structure, has been developed. Such a package does not place any limit to the degree of freedom of designing the shape of hardware. However, any packages sufficiently satisfactory in physical properties and functions required by packages for lithium batteries have not been developed so far. High moistureproof capability or insulating property is a requisite property of packages. Moistureproof capability is particularly important. A packaging laminated structure for forming a package of a lithium ion battery has, as essential components, a base layer, a barrier layer, and a heat-sealable layer. It is confirmed that adhesion between the layers of the packaging laminated structure affects the requisite properties of a package of a lithium ion battery. For example, if adhesion between the barrier layer and the heat-sealable layer is insufficient, external moisture penetrates a package formed from the packaging laminated structure and holding a lithium ion battery module therein into the package, the electrolyte of the

lithium ion battery module reacts with the moisture to produce hydrofluoric acid. The hydrofluoric acid thus produced corrodes the surface of an aluminum layer serving as the barrier layer to cause the delamination of the barrier layer and the heat-sealable layer. Various means for solving such a problem have been proposed.

When sealing a lithium ion battery module in a package, gaps between the tabs of the lithium ion battery and the package must be securely sealed. Conventionally, when a heat-sealable layer having a thermal fusibility is not selected for a tab formed of a metal such as aluminum, SUS or nickel as a package of a lithium ion battery or the heat-sealable layer does not have a thermal fusibility to metals, an adhesive film is bonded to a part of the tab to be heat-sealed. However, any measures have not been taken to prevent the separation of the package from the tabs due to the corrosion of the surfaces of the tabs. Accordingly, the surfaces of the tabs are corroded gradually in a long time, and the heat-sealable layers or the adhesive films of the package bonded to the tabs separate from the tabs and the sealed system of the lithium ion battery is destroyed.

It is an object of the present invention to provide a tab for a lithium ion battery, having a part bonded to a package or an adhesive film, and perfectly resistant to corrosion by the agency of hydrofluoric acid produced by the interaction of an electrolyte and moisture, and a method of forming a corrosion-resistant surface layer on the tab.

[0004]

[Means for Solving the Problems]

The present invention is a lithium ion battery tab including a sealed package of a lithium ion battery having a peripheral part including the part holding the tab sealed by heat-sealing and a lithium ion battery module held in the package comprising at least a base layer, an adhesive layer, a layer treated by a chemical conversion treatment 1, aluminum, a layer treated by a chemical conversion treatment 2 and a heat-sealable layer, wherein the chemical conversion treatment is a phosphate chromate treatment. Specific examples of the chemical conversion treatments further include an Mo, Zr or Ti (non-chromate) treatment and a triazine thiol treatment.

Further, the present invention is a lithium ion battery tab including a sealed package of a lithium ion battery having a peripheral part including the part holding the tab sealed

by heat-sealing and a lithium ion battery module held in the package comprising at least a base layer, an adhesive layer, aluminum, a layer treated by a chemical conversion treatment and a heat-sealable layer of an olefin resin, wherein when heat-sealing the peripheral part of said lithium ion battery, at least the front, the rear and the side surfaces of the part to be heat-sealed are subjected to a chemical conversion treatment, and the chemical conversion treatment is an Mo, Zr or Ti (non-chromate) treatment or a triazine thiol treatment.

[0005]

[Best Mode for Carrying Out the Invention]

Figs. 1(a), 1(b), 1(c), 1(d), 1(e) and 1(f) show a preferred embodiment of a chemical conversion treatment of the lithium ion battery tab and the tab body according to the present invention. Fig. 1(a) is a perspective view of the lithium ion battery module. Fig. 1(b) is a sectional view taken on line  $X_1 - X_1$  in Fig. 1(a). Fig. 1(c) is an enlarged view of a  $Y_1$  part. Fig. 1(d) is a perspective view of the package storing the lithium ion battery. Fig. 1(e) is a sectional view taken on line  $X_2 - X_2$  in Fig. 1(a). Fig. 1(f) is another sectional view taken on line  $X_2 - X_2$  in Fig. 1(a). Figs. 2 shows perspective views of assistance in explaining the pouch package as a package of a lithium ion battery. Figs. 3(a), 3(b), 3(c), 3(d) and 3(e) are perspective views of assistance in explaining an emboss package as a package of a lithium ion battery. Figs. 4(a) and 4(b) are perspective views of assistance in explaining an embossed package of a lithium ion battery. Fig. 4(a) shows locations of a package, an adhesive film and a tab before heat-sealing viewed from one side of the package. Fig. 4(b) is a sectional view of a structure on both sides of the package after heat-sealing. Figs. 5(a), 5(b), 5(c), 5(d) and 5(e) are sectional views of assistance in explaining the bonding of the adhesive film when heat-sealing the package for the lithium ion battery and the tab.

[0006]

Lithium ion batteries are classified by types of packages; the pouch package as shown in Figs. 2(a) and 2(b) and the embossed package as shown in Figs. 3(a), 3(b) and 3(c). The present invention is applicable to either packages.

The peripheral parts of the package 5 is sealed after putting the lithium ion battery module 2 in the package 5 to isolate the lithium ion battery module 2 from



moisture. The tabs made of a metal also need to have a moisture resistance property, and are bonded to the package of the lithium ion battery having the heat-sealable layer which is a film adhesive to metals. However, some resins adhesive to metals have poor workability and are expensive, and hence it is general to form the heat-sealable layer of a generally used polyolefin resin, to place the adhesive film adhesive to both a metal and the heat-sealable layer of the laminated structure forming the package between the tabs and the heat-sealable layer, and to bond the tabs to the heat-sealable layer by heat-sealing.

It is possible that the surfaces of the tabs made of a metal are corroded by hydrofluoric acid (HF) produced in the electrolyte contained in the package and thereby the tabs are separated from the resin layer of the package and, consequently, the electrolytic solution leaks from the package.

The tabs have a thickness in the range of about 50 to about 2000  $\mu\text{m}$ , and a width in the range of about 2.5 to about 20 mm. Possible materials for forming the tabs are Al and Cu (including Ni plating).

Ni is resistant to the corrosive action of hydrofluoric acid, and Al is most subjected to corrosion by hydrofluoric acid.

Further, the inventors of the present invention found through studies that the layer, treated by a chemical conversion treatment, formed on the tabs prevents the dissolution of the tabs in and the corrosion of the same by hydrofluoric acid (HF) produced by the interaction of the electrolyte of the lithium ion battery module and moisture, improves the adhesion (wettability) of the tabs to the innermost layer of the package or the adhesive films, and is effective in stabilizing adhesion between the tabs and the package.

[0007]

As shown in Fig. 1(a) or 1(c), the layer treated by a chemical conversion treatment (hereinafter referred to as "hydrofluoric acid-resistant layer") 4S are formed on at least parts of tab bodies 4M corresponding to the sealed peripheral part of the package. The layers treated by a chemical conversion treatment 4S can be satisfactorily bonded to the innermost layer of a laminated structure forming the

package of the lithium ion battery or the adhesive films by heat-sealing.

The layers resistant to the corrosive action of hydrofluoric acid can be formed by a chemical conversion treatment using a solution prepared by mixing chromium phosphate, chromic acid and such (hereinafter referred to as "phosphate chromate treatment"). As a result, it was found that the adhesion between the adhesive sheet 6 and the tabs 4M was improved for the innermost layer 14 or the tabs 4 of the package of the lithium ion battery as shown in Fig. 1(c) or Fig. 1(d). The present invention was completed based on such finding.

The chemical conversion treatment will be described more specifically. The inventors of the present invention found that a chemical conversion treatment using a resin containing at least a phenolic resin, and a metal of molybdenum, titanium or zirconium, or a metallic salt was also applicable to the object of the present invention in addition to the aforesaid chromate treatment. Further, it was also found that a triazine thiol treatment exhibited a hydrofluoric acid-resistance property as well.

[0008]

In the chromate treatment, for example, a metal sheet, such as an aluminum sheet for tabs, is slit by a slitter to make tab bodies of a predetermined width. The entire surface of the tab body is degreased by wetting the tab body with an organic solvent, surfactant, acid or alkaline solution or by immersing the tab body in an organic solvent, surfactant, acid or alkaline solution. The organic solvent, surfactant, acid or alkaline solution is dried. Then, the metal surface is subjected to a chemical conversion treatment using a chromate solution. The chemical conversion treatment can include the steps of immersing the tab body in the chromate solution, spraying the chromate solution on the tab body, or coating the tab body, with the chromate solution by a roll-coating process. The chromate solution is thus applied to the tab body and the chromate solution on the tab body is dried to perform the entire surface of the tab body by the chemical conversion treatment.

[0009]

Sometimes, the surfaces of the metal sheet are contaminated with oil in a process of forming the metal sheet for the tab body. Sometimes, oil is used for the

protection of the edge of the slit when slitting the metal sheet of a large width into tab bodies of the predetermined width. The tab body is subjected to degreasing to remove oily substances and oils from the tab body.

Acid substances suitable for degreasing are inorganic acids including hydrochloric acid, sulfuric acid, nitric acid, hydrofluoric acid, phosphoric acid, sulfamic acid and such, citric acid, gluconic acid, oxalic acid, tartaric acid, formic acid, hydroxyacetic acid, EDTA (ethylenediamine tetraacetic acid), derivatives of EDTA, ammonium thioglycolate and such.

Alkaline substances suitable for degreasing are sodas including sodium hydroxide ( $\text{NaOH}$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), sodium sesquicarbonate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) and such, silicates including sodium orthosilicate ( $2\text{Na}_2\text{O} \cdot \text{SiO}_2$ , water content: 10 to 40%), sodium metasilicate ( $2\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 9\text{H}_2\text{O}$ ), first sodium silicate ( $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , water content: 42 to 44%) and second silicate ( $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ , water content: 65%), and phosphates including first second and third sodium phosphates ( $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_3\text{PO}_4$ ), sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ), sodium hexa-metaphosphate ( $(\text{NaPO}_3)_6$ ) and sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ).

[0010]

A method of a chemical conversion treatment of the tab body for the lithium ion battery according to the present invention will be described. A metal sheet is slit into tab bodies of a predetermined width, and the tab bodies are subjected to a degreasing process. Subsequently, the degreased tab bodies are subjected to the chemical conversion treatment. Although only parts of the tab bodies corresponding to the sealed peripheral part need to be treated by the chemical conversion treatment, it is desirable to treat the tab bodies entirely by an immersion method, a shower method or a roll-coating method.

[0011]

The phosphate chromate treatment uses a processing solution prepared by mixing a phenolic resin, a chromium fluoride (3) compound and phosphoric acid. The tab bodies are wetted with the processing solution, the processing liquid coating the tab bodies is dried to coat the tab bodies with a film, and the film is baked at a temperature

not lower than 180°C. A suitable weight per unit area of the thus dried film is in the range of 1 to 10 mg/m<sup>2</sup>.

[0012]

The inventors of the present invention found through studies that the formation of a corrosion-resistant film over the surface of an aluminum layer included, as a barrier layer, in a laminated structure for forming the package of the lithium ion battery is very effective in preventing the dissolution of the surface of the aluminum layer and the corrosion of the same by hydrofluoric acid (HF) produced by the interaction of the electrolyte of the lithium ion battery module and moisture, in improving the adhesion (wettability) of the surface of the aluminum layer, and in stabilizing adhesion between the aluminum layer and the innermost layer of the laminated structure. The inventors found also that the layer treated by a chemical conversion treatment, i.e., a film resistant to the corrosive action of hydrofluoric acid, formed on the tab has an excellent effect.

[0013]

The chemical conversion treatment of the tab bodies after degreasing is carried out by wetting the tab bodies entirely with a processing solution prepared by mixing a phenolic resin, a chromium fluoride (3) compound and phosphoric acid by an immersion method, a shower method or a roll-coating method. Then, the processing liquid applied to the tab bodies is dried to form a film on the tab bodies, and the film is hardened by heating using hot air, far-infrared radiation or the like. A desirable weight per unit area of the film as dried is on the order of 10 mg/m<sup>2</sup>.

[0014]

As in the phosphate chromate treatment, a metal sheet for tabs is slit to make tab bodies of a predetermined width. The entire surface of the tab body is wetted by immersing the tab body with a resin containing at least a phenolic resin, and a metal of molybdenum, titanium or zirconium, or a metallic salt by an immersion method, a shower method or a roll-coating process. Then, the processing liquid applied to the tab bodies is dried to form a film on the tab bodies, and the film is hardened by heating using hot air, far-infrared radiation or the like. A desirable weight per unit area of the film as dried is on the order of 10 mg/m<sup>2</sup>.

[0015]

A metal sheet for tabs is slit to make tab bodies of a predetermined width. The entire surface of the tab body is decreased and a triazine thiol film is formed thereon by electrolytic polymerization using a solution containing triazine thiol.

[0016]

A material for forming the package 10 of the lithium ion battery will be described hereinafter. As shown in Fig. 4(a), the package 5 comprises at least a base layer 11, a barrier layer 12 and a heat-sealable layer 14. Those component layers of the laminated structure are laminated by a dry-lamination process, a sandwich-lamination process, an extrusion-lamination process and/or a thermal-lamination process. An intermediate layer 13 may be interposed between the barrier layer 12 and the heat-sealable layer 14 as shown in Fig. 4(b).

[0017]

The outermost layer is formed of an oriented polyester or nylon film. Suitable polyester resins for forming the oriented polyester film include polyethylene terephthalate resins, polybutylene terephthalate resins, polyethylene naphthalate resins, polybutylene naphthalate resins, polyester copolymers and polycarbonate resins. Suitable polyamide resins for forming the oriented nylon film include nylon 6, nylon 6, 6, copolymers of nylon 6 and nylon 6, 6, nylon 6, 10 and polymethaxylilene adipamide (MXD6).

[0018]

When the lithium ion battery is used on hardware, the outermost layer directly touches the hardware. Therefore, it is desirable to form the outermost layer of an intrinsically insulating resin. Since a film forming the outermost layer has pinholes and pinholes will be formed in the film during processing, the thickness of the outermost layer must be 6  $\mu\text{m}$  or above. Preferably, the thickness of the outermost layer is in the range of 12 to 30  $\mu\text{m}$ .

[0019]

The outermost layer may be a laminated film in view of providing the outermost layer with a high pinhole-resistant property and an improved insulating ability.

Preferably, the outermost layer includes at least one resin layer consisting of two or more layers each having a thickness of 6  $\mu\text{m}$  or above, preferably, in the range of 12 to 25  $\mu\text{m}$ . The following laminated structures 1) to 8) are examples of the laminated outermost layer.

- 1) Oriented polyethylene terephthalate resin layer/Oriented nylon layer
- 2) Oriented nylon layer/Oriented polyethylene telephthalate resin layer

To improve the mechanical aptitude (stability when passed through processing machines and a packaging machine) and surface protecting ability (heat resistance and electrolyte resistance) of the packaging sheet and to reduce friction between a die and the outermost layer when forming the embossed package body as a secondary process, it is preferable that the outermost layer consists of a plurality of layers and the surface of the outermost layer is coated with a coating of a fluorocarbon resin, an acrylic resin, a silicone resin or a mixture thereof. The outermost layer may be any one of the following laminated films.

3) Fluorocarbon resin layer/Oriented resin layer (the fluorocarbon resin layer may be a fluorocarbon resin film or a film formed by spreading a liquid fluorocarbon resin in a film and drying the same.)

4) Silicone resin layer/Oriented polyethylene telephthalate resin layer (the silicone resin layer may be a silicone resin film or a film formed by spreading a liquid silicone resin in a film and drying the same.)

5) Fluorocarbon resin layer/Oriented polyethylene telephthalate resin layer/Oriented nylon layer

6) Silicone resin layer/Oriented polyethylene telephthalate resin layer/Oriented nylon layer

7) Acrylic resin layer/Oriented nylon layer (the acrylic resin layer may be an acrylic resin film or a film formed by spreading an acrylic resin and drying the same.)

8) Acrylic resin layer + polysiloxane graft acrylic resin layer/Oriented nylon layer (the acrylic resin layer may be an acrylic resin film or a film formed by spreading an acrylic resin and drying the same.)

[0020]

The laminated structure for forming the package of the lithium ion battery may be formed by a dry-lamination process, a thermal-lamination process, an extrusion-lamination process, a sandwich-lamination process and or a coextrusion-lamination process.

[0021]

The barrier layer 12 of the package of the lithium ion battery prevents the penetration of steam into the lithium ion battery. To stabilize the workability (ease of fabricating pouches or embossing) and to provide the barrier layer 12 with pinhole resistance, the barrier layer 12 has a thickness of 15  $\mu\text{m}$  or above and is formed from a foil of a metal, such as aluminum or nickel, or a film coated with an inorganic compound, such as silicon dioxide or alumina, by evaporation. Preferably, the barrier layer 12 is an aluminum foil of a thickness in the range of 15 to 80  $\mu\text{m}$ .

The inventors of the present invention made studies to reduce pinholes and to prevent the cracking of an embossed battery package and found that an aluminum having an iron content in the range of 0.3 to 9.0% by weight, preferably, in the range of 0.7 to 2.0% by weight is more satisfactory in ductility than aluminum not containing any iron, and an aluminum foil of such aluminum is less subjected to the formation of pinholes when a laminated sheet including the aluminum foil of such aluminum is folded and is more capable of facilitating forming walls of an embossed battery package than an aluminum foil of aluminum not containing any iron. Aluminum having an iron content less than 0.3% by weight is unable to form a satisfactorily pinhole-resistant foil and does not have improved formability. Aluminum having an iron content exceeding 9.0% by weight is unsatisfactory in flexibility and affects adversely to the workability of the laminated structure in forming a pouch.

[0022]

The flexibility, stiffness and hardness of an aluminum foil formed by cold rolling are dependent on annealing conditions. It is preferably to use soft, properly annealed aluminum foils in comparison with those treated by a hardening process and not annealed.

Annealing conditions that affect the flexibility, stiffness and hardness of aluminum foils may be properly determined according to the required workability (ease of forming

pouches or embossed packages) of the laminated structure. For example, to prevent the formation of creases or pinholes in making a package by an embossing process, a slightly or completely annealed soft aluminum foil is more preferable than a hard aluminum foil.

[0023]

It is possible that the surface of the aluminum foil, particularly, aluminum oxide covering the surface of the aluminum foil is dissolved in or is corroded by hydrofluoric acid (HF) produced by the interaction of the electrolyte of the lithium ion battery and moisture. The inventors of the present invention found through studies that the formation of a corrosion-resistant film over the surface of an aluminum layer included in a laminated structure is very effective in preventing the dissolution of the surface of the aluminum layer and the corrosion of the same by hydrofluoric acid, in improving the adhesion (wettability) of the surface of the aluminum layer, and in stabilizing adhesion between the aluminum layer and the innermost layer.

[0024]

As shown in Fig. 1(e), the innermost layer (heat-sealable layer) is formed of a material such that the innermost layer of a part of the laminated structure for forming the package of the lithium ion battery can be bonded to the heat-sealable layer of another part of the same laminated structure and to the metal tabs by heat-sealing and is not subjected to quality change and deterioration due to the injurious effect of the contents of the package thereon. It was found through studies that a satisfactory innermost layer has a thickness of 10  $\mu\text{m}$  or above, preferably, in the range of 20 to 100  $\mu\text{m}$ , and is formed of a material including at least one of unsaturated carboxylic acid graft polyolefin resins including unsaturated carboxylic acid graft polyethylene resins, unsaturated carboxylic acid graft polypropylene resins and unsaturated carboxylic acid graft polymethyl-pentene resins, and having a melting point of 80°C or above and a Vicat softening point of 70°C or above, copolymers of metal ion crosslinked polyethylene resins, ethylene or propylene, and acrylic acid or methacrylic acid, and modified resins obtained by modifying those resins.

[0025]

The heat-sealable layer 14 may be formed of a material not adhesive to metals,



such as a polyolefin resin. When the heat-sealable layer 14 is formed of a material not adhesive to metals, the tabs 4 and the package can be perfectly bonded and the package can be sealed by placing a thermoadhesive film (hereinafter referred to as "adhesive film") having a thickness of 15  $\mu\text{m}$  or above and formed of a unsaturated carboxylic acid graft polyolefin resin, a metal-crosslinked polyethylene resin, or a copolymer of ethylene or propylene, and acrylic acid or methacrylic acid between the electrodes and the innermost layer as shown in Fig. 1(f).

Adhesive films 6 adhesive to both the tabs 4 and the heat-sealable layer 14 may be placed between the tabs 4 and the innermost layers 14 as shown in Figs. 5(a), 5(b) and 5(c), or may be wound around predetermined parts of the tabs 4 as shown in Figs. 5(d), 5(e) and 5(f).

Possible materials for forming the adhesive film 6 are unsaturated carboxylic acid graft polyolefin resins, metal-crosslinked polyethylene resins, and copolymers of ethylene or propylene, and acrylic acid or methacrylic acid.

The heat-sealable layer 14 of the laminated structure may be a single layer of the aforesaid resin or a plurality of layers including a layer of the aforesaid resin.

[0026]

The unsaturated carboxylic acid graft polyolefin resins are satisfactory in adhesion to the electrodes, heat resistance, cold resistance and workability (ease of fabricating pouches or embossing). If the thickness of the innermost layer is less than 20  $\mu\text{m}$ , gaps are formed between the electrodes and the innermost layers of opposite parts of the laminated structure when the innermost layers of the opposite parts of the laminated structure are bonded together by heat-sealing and the package cannot be perfectly sealed. Even if the thickness of the innermost layer 14 is increased beyond 100  $\mu\text{m}$ , the sealing effect of the innermost layer 14 does not increase accordingly, and the thickness of the laminated structure increases, which is contrary to the object of the present invention to form the lithium ion battery in a small size.

If the resin forming the innermost layer 14 has an excessively low melting point and an excessively low Vicat softening point, the heat resistance and cold resistance of the innermost layer 14 is unsatisfactory, adhesion between films and adhesion between a

film and the electrodes are insufficient. Consequently, the sealed-parts of the package, such as a pouch, would be open. The foregoing unsaturated carboxylic acid graft polymers may be used individually or a mixture having satisfactory properties of some of those polymers may be used.

[0027]

Each of the component layers of the laminated structure according to the present invention may be treated by a surface activation treatment, such as a corona discharge treatment, a blasting treatment, an oxidation treatment or an ozone treatment, to improve and stabilize the film-forming property, lamination property and workability (ease of forming pouches or embossing).

[0028]

Possible processes of forming the outermost layer, the barrier layer, the intermediate layer and the outermost layer of the laminated structure include a T-die process, an inflation process and a coextrusion process. When necessary, a secondary film may be formed by a coating process, an evaporation process, an ultraviolet curing process or an electron beam curing process.

Possible processes of laminating those layers include a dry-lamination process, an extrusion-lamination process, a coextrusion-lamination process and a thermal-lamination process.

[0029]

When laminating the component layers of the laminated structure by a dry-lamination process, polyester resins, polyethylene imine resins, polyether resins, cyanoacrylate resins, polyurethane resins, organic titanium compounds, polyether polyurethane resins, epoxy resins, polyester polyurethane resins, imide resins, isocyanate resins, polyolefin resins and silicone resins may be used.

An additive may be added to those materials for forming the adhesive layers to improve the chemical resistance and solvent resistance of the adhesive layers. Possible additives include at least one of silicon dioxide, calcium carbonate, zinc, minium, lead suboxide, lead dioxide, lead cyanamide, zinc chromate, barium potassium chromate and barium zinc chromate. Silicon dioxide, calcium carbonate, zinc, minium, lead suboxide,

lead dioxide, lead cyanamide, zinc chromate, barium potassium chromate and barium zinc chromate are capable of absorbing and adsorbing hydrofluoric acid produced by interaction between an electrolyte and moisture and have an effect of preventing the corrosion of the layers, particularly, the barrier layer (aluminum layer) by hydrofluoric acid.

[0030]

An adhesive layer of a thickness on the order of 1  $\mu\text{m}$  may be formed on the surface of the layer or the surface of the layer may be finished by a surface activation treatment, such as an ozone treatment, to enhance and stabilize the adhesion between the layers when laminating the layers by the extrusion-lamination process. Possible materials for forming the adhesive layer are polyester resins, polyether resins, polyurethane resins, polyether polyurethane resins, polyester polyurethane resins, isocyanate resins, polyolefin resins, polyethylene imine resins, cyanoacrylate resins, organic titanium compounds, epoxy resins, imide resins, silicone resins, modified resins obtained by modifying those resins and mixtures of some of those resins.

An unsaturated carboxylic acid graft polyolefin resin may be used as an adhesive for bonding together the layers by the extrusion-lamination process or the thermal-lamination process to improve adhesion between the layers and to enhance the chemical resistance of the laminated structure.

[0031]

[Examples]

Examples of the tabs of the lithium ion battery and a method of processing the tab bodies by the chemical conversion treatment will be described.

The following conditions are common to examples of the present invention and comparative examples.

(1) The tab as a positive electrode is made of nickel and the tab as a negative electrode is made of aluminum. The tabs are 8 mm in width, 50 mm in length and 100  $\mu\text{m}$  in thickness.

(2) Pouches are of a pillow type, are 60 mm in width and 80 mm in length, and have sealed fins of 5 mm in width.

(3) Embossed packages are of a one-side pressed type provided with a hollow

part of 35 mm in width, 50 mm in length and 3.5 mm in depth, a flange (sealed part) of 5 mm in width.

(4) The tabs cut in a size for attachment to the lithium ion battery module were subjected to the degreasing process and the chemical conversion treatment. In a practical tab manufacturing process, long strips obtained by slitting a metal sheet for forming the tab bodies are subjected to the degreasing process and the chemical conversion treatment.

[Example 1] (Pouch type)

1. Tab bodies were immersed in a 0.1 N sulfuric acid solution for 10 s (second), the tab bodies were cleaned with water and the thus cleaned tab bodies were dried. Subsequently, the tab bodies were immersed in a solution containing a phenolic resin, a chromium fluoride (3) compound and phosphoric acid for 5 s. The tab bodies wetted with the solution were dried with hot air. The dried tab bodies were heated by a far infrared heater to heat the substance coating the tab bodies at 190°C to complete tabs. The tabs were bonded to the end of a lithium cell to complete a lithium ion battery module.

2. A laminated structure for forming the package was made by the following procedure.

One of the surfaces of a 20  $\mu\text{m}$  thick aluminum foil was subjected to a chemical conversion treatment. A 16  $\mu\text{m}$  thick oriented polyester resin film was laminated to the other surface of the aluminum foil by a dry-lamination process. A 50  $\mu\text{m}$  thick film of an acid-denatured polypropylene resin was laminated to the surface treated by the chemical conversion treatment of the aluminum foil by a dry-lamination process to obtain a sample laminated structure. The sample laminated structure was processed to form a pouch to obtain a package 1.

3. The battery module was put in the pouch, and an open end part of the pouch was sealed in a sealed fin by heat-sealing so that the tabs extend through the sealed fin to obtain a sample lithium ion battery in Example 1.

[Example 2] (Embossed package type)

1. Tab bodies were immersed in a 1.0 N sodium hydroxide solution for 10 s, the tab bodies were cleaned with water and the thus cleaned tab bodies were dried.

Subsequently, the tab bodies were immersed in a solution containing a phenolic resin, a chromium fluoride (3) compound and phosphoric acid for 5 s. The tab bodies wetted with the solution were dried with hot air. The dried tab bodies were heated by a far infrared heater to heat the substance covering the tab bodies at 190°C to complete tabs. The tabs were bonded to a lithium cell to obtain a lithium ion battery module in Example 2.

2. Both the surfaces of a 40  $\mu\text{m}$  thick aluminum foil were subjected to a chemical conversion treatment. A 25  $\mu\text{m}$  thick oriented nylon film was laminated to one of the surfaces of the aluminum foil by a dry-lamination process. A 30  $\mu\text{m}$  thick polypropylene resin film having a density of 0.921 was bonded with a 15  $\mu\text{m}$  thick layer of an acid-denatured polypropylene resin to the other surface of the aluminum foil by sandwich-lamination to form a primary laminated structure. The primary laminated structure was heated at a temperature not lower than the softening point of the acid-denatured polypropylene resin with hot air to obtain a sample secondary laminated structure. The sample secondary laminated structure was pressed to form an embossed package body and was cut to form a lid to obtain a package in Example 2.

The tabs held between 100  $\mu\text{m}$  thick adhesive films of an acid-denatured polypropylene resin were attached to a battery module, the battery module was placed in the hollow part of the embossed package body, the lid was put on the embossed package body and a peripheral part of the lid was bonded to the embossed package body by heat-sealing to obtain a sample lithium ion battery in Example 2.

[Example 3] (Pouch type)

1. Tab bodies were immersed in acetone for 10 s, the tab bodies were dried. Subsequently, the tab bodies were immersed in a first solution containing a phenolic resin, acrylic resin, and hydrogen fluoride and molybdenum, a second solution containing a phenolic resin, acrylic resin, and hydrogen fluoride and titanium, and a third solution containing a phenolic resin, acrylic resin and zirconium. The tab bodies wetted with those solutions were dried with hot air. The dried tab bodies were heated to heat the substances coating the tab bodies at 180°C to complete tabs. The tabs were bonded to lithium cells to provide the first, second and third lithium ion battery modules

in Example 3.

2. A laminated structure for forming the package was made by the following procedure.

One of the surfaces of a 20  $\mu\text{m}$  thick aluminum foil was subjected to a chemical conversion treatment. A 16  $\mu\text{m}$  thick oriented polyester resin film was laminated to the other surface of the aluminum foil by a dry-lamination process. A 50  $\mu\text{m}$  thick film of an acid-denatured polypropylene resin was laminated to the surface treated by the chemical conversion treatment of the aluminum foil by a dry-lamination process to obtain a sample laminated structure. The sample laminated structure was processed to form a pouch to obtain a package in Example 3.

3. The first, the second and the third lithium ion battery module 3 were put in the packages in Example 3, and open end parts of the packages were sealed together with tabs to obtain sample lithium ion batteries in Example 3.

[Example 4] (Embossed typr)

1. Tab bodies were immersed in acetone for 10 s, the tab bodies were dried. Subsequently, the tab bodies were immersed in a first solution containing a phenolic resin, acrylic resin, and hydrogen fluoride and molybdenum, a second solution containing a phenolic resin, acrylic resin, and hydrogen fluoride and titanium, and a third solution containing a phenolic resin, acrylic resin and zirconium. The tab bodies wetted with those solutions were dried with hot air. The dried tab bodies were heated to heat the substances coating the tab bodies at 180°C to complete tabs. The tabs were bonded to lithium cells to obtain the first, second and third lithium ion battery modules in Example 4.

2. Both the surfaces of a 40  $\mu\text{m}$  thick aluminum foil were subjected to a chemical conversion treatment. A 25  $\mu\text{m}$  thick oriented nylon film was laminated to one of the surfaces of the aluminum foil by a dry-lamination process. A 30  $\mu\text{m}$  thick molten resin film of a MDPE resin, as a heat-sealable layer, was extruded on the other surface of the aluminum foil, processing the surface of the molten resin film to be bonded to the aluminum foil by an ozone treatment to form a laminated structure. The laminated structure was heated at a temperature not lower than the softening point of the MDPE resin to obtain a sample laminated structure. The sample laminated structure

was pressed to form an embossed package body and was cut to form a lid to obtain a package in Example 4.

3. The lithium ion battery module in Example 4 provided with the tabs held between 100  $\mu\text{m}$  thick adhesive films of an acid-denatured LLDPE resin was put in the embossed package body of the package 4, the lid was put on the embossed package body, and a peripheral part of the lid was bonded to the flange of the embossed package body to form a sealed part by heat-sealing to obtain the first, second and third sample lithium ion batteries in Example 4.

[Example 5] (Pouch type)

1. Tab bodies were immersed in a 0.1 N sulfuric acid solution for 10 s, the tab bodies were cleaned with water and the thus cleaned tab bodies were dried. Subsequently, the tab bodies were subjected to an electroplating process using a triazine thiol solution to obtain plated tabs. The plated tabs were bonded to a lithium cell to complete a lithium ion battery module in Example 5.

2. A laminated structure for forming the package was made by the following procedure.

One of the surfaces of a 20  $\mu\text{m}$  thick aluminum foil was subjected to a chemical conversion treatment. A 16  $\mu\text{m}$  thick oriented polyester resin film was laminated to the other surface of the aluminum foil by a dry-lamination process. A 50  $\mu\text{m}$  thick film of an acid-denatured polypropylene resin was laminated to the surface treated by the chemical conversion treatment of the aluminum foil by a dry-lamination process to obtain a sample laminated structure. The sample laminated structure was processed to form a pouch to obtain a lithium ion battery in Example 5.

3. The lithium ion battery module in Example 5 was put in the pouch in Example 5, and an open end part of the pouch was sealed together with tabs to form a sealed part by heat-sealing to obtain a sample lithium ion battery in Example 5.

[Example 6] (Embossed type)

1. Tab bodies were immersed in a 0.1 N sulfuric acid solution for 10 s, the tab bodies were cleaned with water and the thus cleaned tab bodies were dried. Subsequently, the tab bodies were subjected to an electroplating process using a triazine thiol solution

to obtain plated tabs. The plated tabs were bonded to a lithium cell to complete a lithium ion battery module in Example 6.

2. Both the surfaces of a 40  $\mu\text{m}$  thick aluminum foil were subjected to a chemical conversion treatment. A 25  $\mu\text{m}$  thick oriented nylon film was laminated to the one of the surfaces of the aluminum foil by a dry-lamination process. A 30  $\mu\text{m}$  thick molten resin film of a MDPE resin, as a heat-sealable layer, was extruded on the other surface of the aluminum foil, processing the surface of the molten resin film to be bonded to the aluminum foil by an ozone treatment to form a laminated structure. The laminated structure was heated at a temperature not lower than the softening point of the MDPE resin to obtain a sample laminated structure. The sample laminated structure was pressed to form an embossed package body and was cut into a predetermined size to form a lid to obtain a package in Example 6.

3. The lithium ion battery module in Example 6 provided with the tabs held between 100  $\mu\text{m}$  thick adhesive films of an acid-denatured LLDPE resin was put in the embossed package body in Example 6, the lid was put on the embossed package body, and a peripheral part of the lid was bonded to the flange of the embossed package body to form a sealed part by heat-sealing to obtain a sample lithium ion battery in Example 6.

[0032]

[Comparative Example 1] (Pouch typr)

1. Tabs were immersed in a 0.1 N sulfuric acid solution for 10 s, the tabs were cleaned with water and the thus cleaned tabs were dried. The tabs were bonded to the end of a lithium cell to complete a lithium ion battery module in Comparative example 1.

2. A laminated structure for forming the package was made by the following procedure.

One of the surfaces of a 20  $\mu\text{m}$  thick aluminum foil was subjected to a chemical conversion treatment. A 16  $\mu\text{m}$  thick oriented polyester resin film was laminated to the other surface of the aluminum foil by a dry-lamination process. A 50  $\mu\text{m}$  thick film of an acid-denatured polypropylene resin was laminated to the surface treated by the chemical conversion treatment of the aluminum foil by a dry-lamination process to



obtain a sample laminated structure. The sample laminated structure was processed to form a pouch to obtain a package in Comparative example 1.

3. The battery module in Comparative example 1 was put in the pouch in Comparative example 1 and an open end part of the pouch was sealed to form a sealed fin so that the tabs extends through the sealed fin to obtain a sample lithium ion battery in Comparative example 1.

[Comparative Example 2] (Embossed typr)

1. Tab bodies were immersed in a 0.1 N sulfuric acid solution for 10 s, the tab bodies were cleaned with water and the thus cleaned tab bodies were dried to obtain tabs. The tabs were bonded to a lithium cell to complete a lithium ion battery module in Comparative example 2.

2. Both the surfaces of a 40  $\mu\text{m}$  thick aluminum foil were subjected to a chemical conversion treatment. A 25  $\mu\text{m}$  thick oriented nylon film was laminated to one of the surfaces of the aluminum foil by a dry-lamination process. A 30  $\mu\text{m}$  thick molten resin film of a MDPE resin, as a heat-sealable layer, was extruded on the other surface of the aluminum foil, processing the surface of the molten resin film to be bonded to the aluminum foil by an ozone treatment to form a laminated structure. The laminated structure was heated at a temperature not lower than the softening point of the MDPE resin to obtain a sample laminated structure. The sample laminated structure was pressed to form an embossed package body and was cut to form a lid to obtain a package in Comparative example 2.

3. The tabs held between 100  $\mu\text{m}$  thick adhesive films of an acid-denatured LLDPE resin were attached to a battery module, the battery module in Comparative example 2 was placed in the hollow part of the embossed package body of the package in Comparative example 2, the lid was put on the embossed package body and a peripheral part of the lid was bonded by heat-sealing to obtain a sample lithium ion battery in Comparative example 2.

<Evaluation>

[0033]

The sample lithium ion batteries were held with the tabs extended downward, 5 g of an electrolyte prepared by adding 1 mol lithium phosphate hexafluoride to a 1 : 1 : 1

mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate was put in each of the sample pouches and embossed packages, and the sample lithium batteries were held at 85°C for thirty days. Then, the sample lithium ion batteries were examined visually to see if the contents were leaking from the packages through parts around the tabs.

#### <Test Results>

[0034]

[0034]

None of the sample lithium ion batteries in Examples 1 to 6 leaked, and parts around the tabs of aluminum of the sample lithium ion batteries in Examples 1 and 2 were satisfactorily sealed. Parts around the negative tabs of aluminum of 400 sample lithium ion batteries among 1000 sample lithium ion batteries in Comparative example 1 leaked. Similarly, parts around the negative tabs of aluminum of 500 sample lithium ion batteries among 1000 sample lithium ion batteries in Comparative example 2 leaked.

[0035]

#### [Advantages of the Invention]

By bonding the layer treated by a chemical conversion treatment to the surface of the tabs of the lithium ion battery, the tabs are surely bonded to the package, the dissolution and corrosion of the surfaces of the tabs by hydrofluoric acid produced by interaction between the electrolyte of the lithium ion battery and moisture penetrated the package can be prevented, and sealing of parts around the tabs of the package is stabilized.

#### [Brief Description of the Drawings]

[Fig. 1]

A view of a lithium ion battery and an example of a chemical conversion treatment with tab bodies. Fig. 1(a) shows perspective views of the lithium ion battery module and a package. Fig. 1(b) is a sectional view taken on line  $X_1 - X_1$  in Fig. 1(a). Fig. 1(c) is an enlarged view of a  $Y_1$  part. Fig. 1(d) is a sectional view of the package holding the lithium ion battery therein. Fig. 1(e) is a sectional view taken on line  $X_2 - X_2$ . Fig. 1(f) is another sectional view taken on line  $X_2 - X_2$  in Fig. 1(a).

[Fig. 2]

A perspective view of assistance in explaining a pouch as a package for a lithium ion battery.

[Fig. 3]

A perspective view of assistance in explaining an embossed package as a package for a lithium ion battery.

[Fig. 4]

A sectional view of assistance in explaining an example of the construction of laminated structures for forming packages for lithium ion batteries according to the present invention. Fig. 4(a) shows a package, an adhesive film, and tabs before heat-sealing viewed from one side of the package. Fig. 4(b) shows the construction after heat-sealing viewed from both sides of the package.

[Fig. 5]

A perspective view of assistance in explaining methods of putting adhesive films between a package for a lithium ion battery and tabs.

[Reference Characters]

- 1: Lithium ion battery
- 2: Lithium ion battery module
- 3: Cell (storage)
- 4: Tab (electrode)
- 4M: Tab body
- 4S: Layer treated by chemical conversion treatment (tab)
- 5: Package
- 6: Adhesive film
- 7: Recess
- 8: Side wall
- 9: Sealed part
- 10: Laminated structure forming package
- 11: Base layer

12: Barrier layer

13: Adhesive resin layer

14: Heat-sealable layer

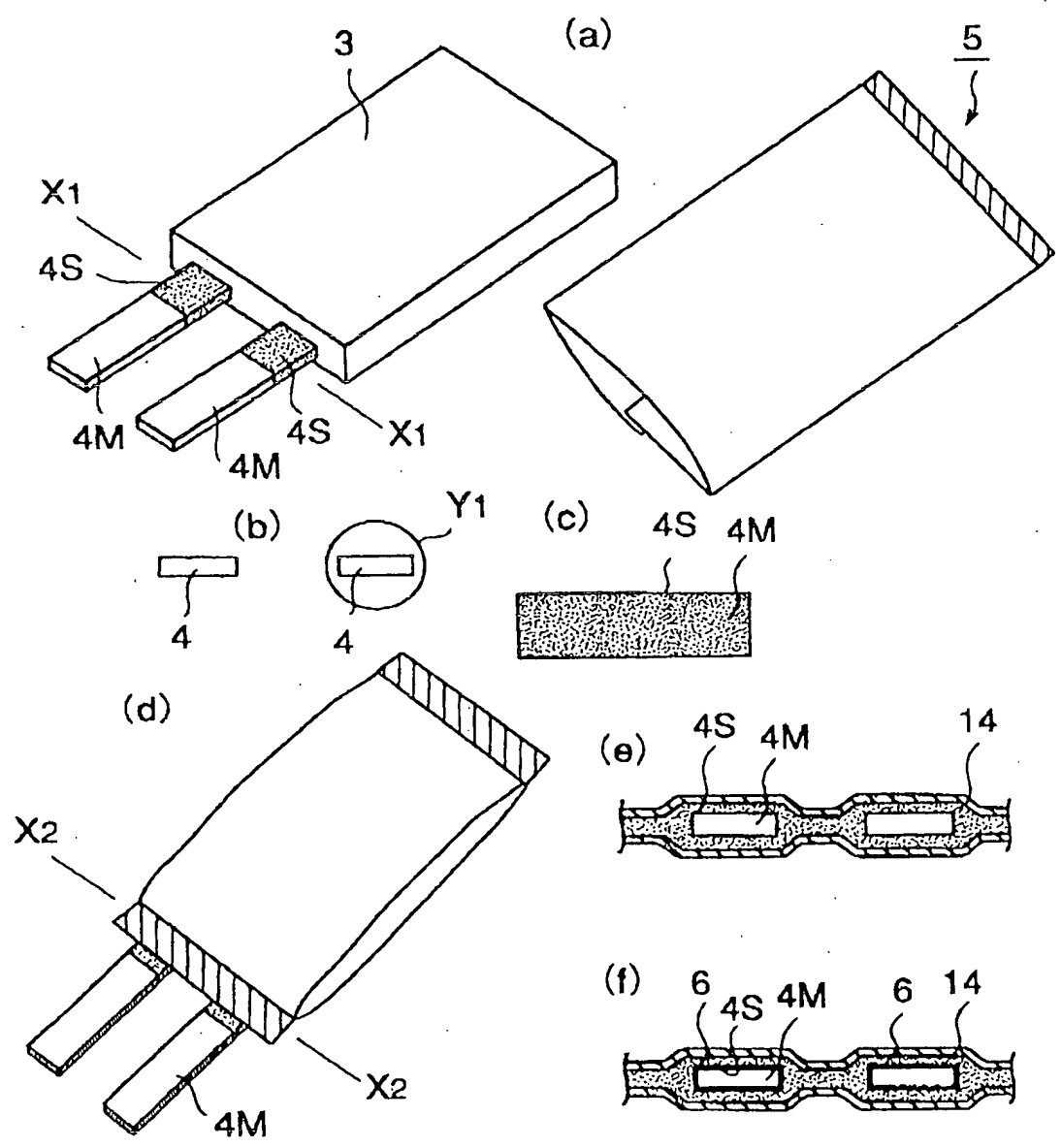


Fig. 1

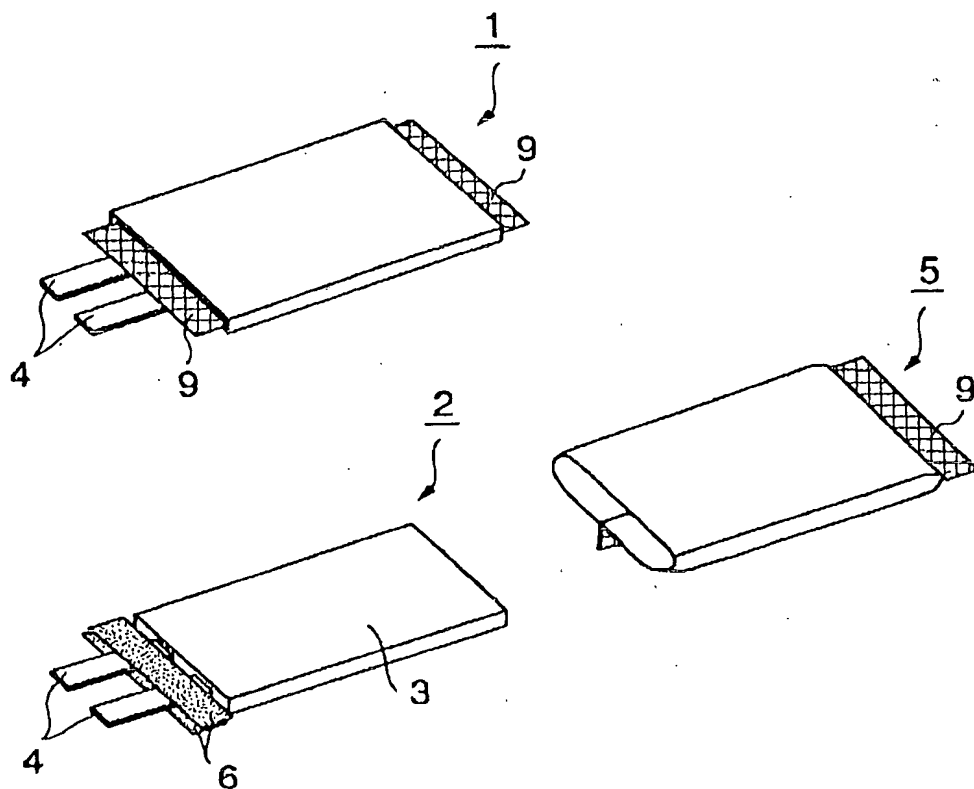


Fig. 2

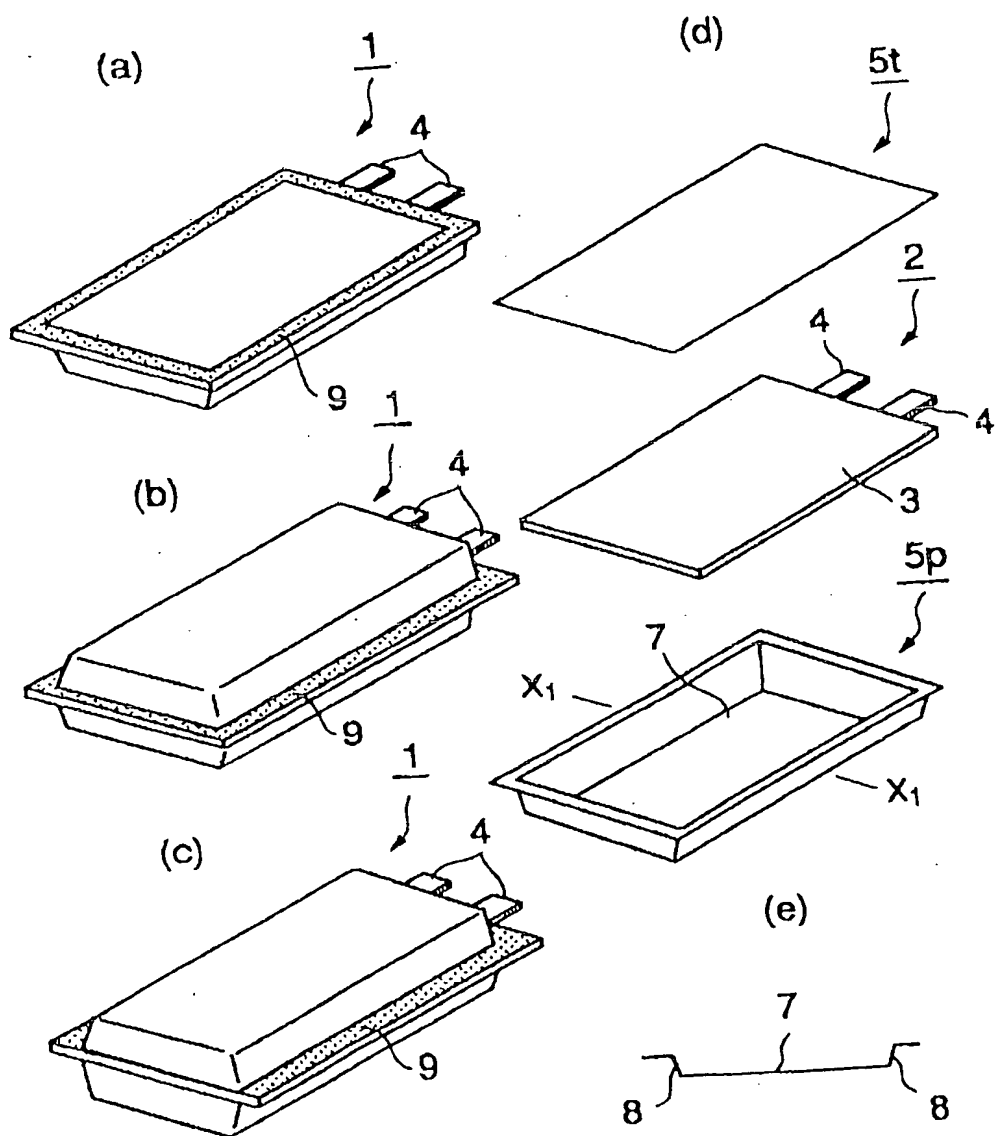


Fig. 3

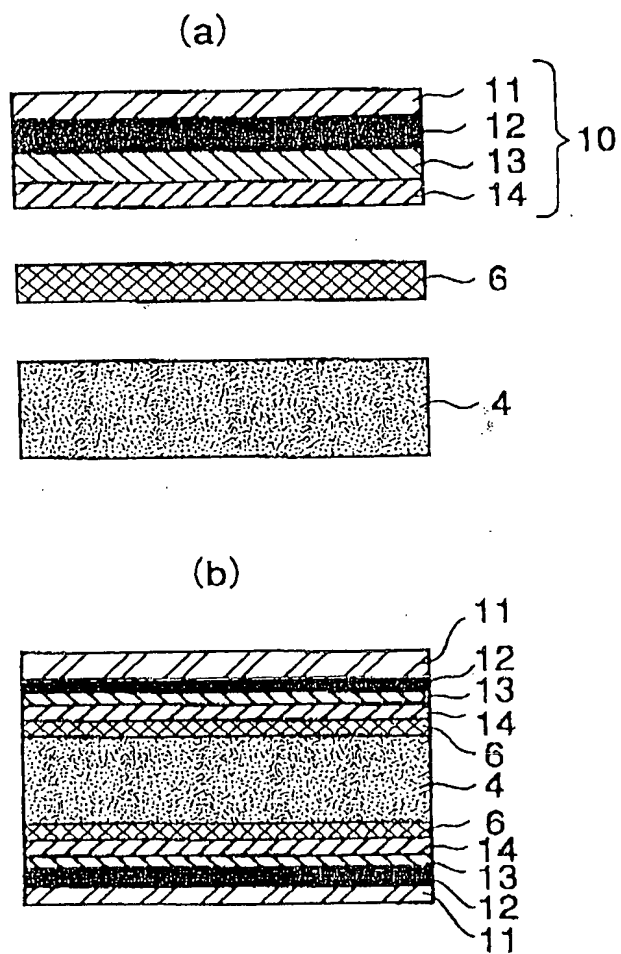


Fig. 4



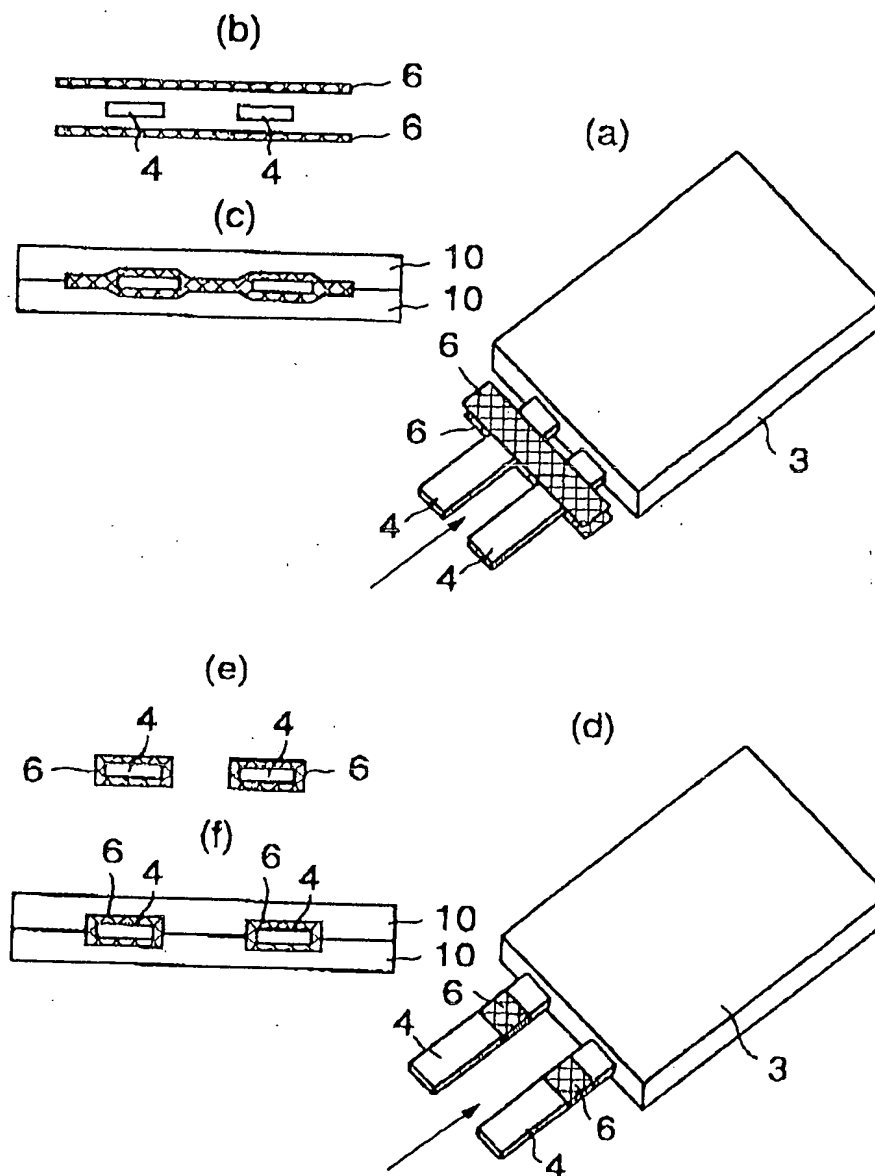
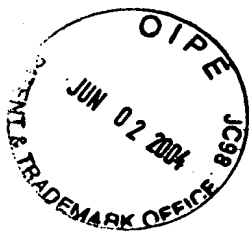


Fig. 5

[Document Type]      ABSTRACT

[Abstract]

[Object]

To provide a tab for a lithium ion battery, having a part bonded to a package or an adhesive film, and perfectly resistant to corrosion by the agency of hydrofluoric acid produced by the interaction of an electrolyte and moisture, and a method of forming a corrosion-resistant surface layer on the tab.

[Means for Solving the Problems]

A lithium ion battery tab including a sealed package of a lithium ion battery having a peripheral part including the part holding the tab sealed by heat-sealing and a lithium ion battery module held in the package comprising at least a base layer, an adhesive layer, aluminum, a layer treated by a chemical conversion treatment and a heat-sealable layer, wherein at least the front, rear and side surfaces of the part to be heat-sealed are treated by a chemical conversion treatment. The chemical conversion treatment is a phosphate chromate treatment. Specific examples of the chemical conversion treatments further include an Mo, Zr or Ti (non-chromate) treatment and a triazine thiol treatment.

[Selected Drawing]

Fig. 1